The Relation of the Anilides of Orthosulphobenzoic Acid.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

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JOSEPH RUFUS HUNTER.

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The investigation described in the following pages was undertaken at the suggestion of Professor Ira Remsen, and carried on under his constant supervision. The author gladly avails himself of this opportunity to express to him, as well as to Professor H. N. Morse, his sincere gratitude for the assistance they have freely rendered during its progress.

THE RELATION OF THE ANILIDES OF ORTHO-SULPHOBENZOIC ACID.

I. Introduction.

Orthosulphobenzoic acid was first prepared by Remsen and Fahlberg[1] in the year 1879, by oxidizing orthotoluenesulphoneamide by potassium permanganate in alkaline solution.

It was further investigated by Remsen and Dohme[2], who prepared a large number of its salts, as well as the chloride obtained by the action of phosphorus pentachloride, on the acid ammonium salt. They obtained crystals of the chloride; and from its ability to form chloro-ethers of the general formula,

$$C_6H_4 \begin{cases} COOR \\ SO_2Cl \end{cases},$$

in which the chlorine could be easily replaced by hydroxyl forming an acid of the structure $C_6H_4 \begin{cases} COOR \\ SO_2OH \end{cases}$, they represented its structure by the formula,

$$C_6H_4 \begin{cases} COCl \\ SO_2Cl \end{cases}.$$

No evidence was obtained that this chloride was not homogeneous.

Remsen and Coates[3], in 1891, studied the action of aniline on this chloride, and obtained two isomeric anilides quite different in properties, and an anil. From this work it seemed quite evident that there were two isomeric chlorides, from which the anilides were derived.

Later, Remsen and Kohler[4] obtained one of these chlorides pure, in crystalline form, while the other one was an oil, always containing more or less of the crystalline variety. It was further shown in this investigation that the anil and the fusible anilide described by Remsen and Coates,[5] were deri-

1 Am. Chem. J., **1**, 433.
2 Ibid, **11**, 332.
3 Ibid, **17**, 311.
4 Ibid, **17**, 330.
5 *Loc. cit.*

vatives of the symmetrical (or solid) chloride, $C_6H_4 \begin{matrix} COCl \\ SO_2Cl \end{matrix}$, while from the unsymmetrical (or liquid) chloride, for which the formula $C_6H_4 \begin{matrix} CCl_2 \\ SO_2 \end{matrix} O$ had been proposed, the infusible anilide, together with some of the fusible one, was obtained.

The liquid chloride was first obtained pure by Remsen and Saunders,[1] who obtained it as thin white needles, by crystallizing from petroleum ether (boiling point 80°) at low temperatures. The melting-point of this chloride was found to be 21.5°–22.5° uncorr., that of the solid chloride 76°–77° uncorr.

Mr. S. R. McKee, working in this laboratory, has recently shown that both anilides are formed by the action of aniline on the *pure* low melting (or liquid) chloride, in ether solution.

Remsen and Kohler's work showed that the structure of the fusible anilide is represented by the formula,

$$C_6H_4 \begin{matrix} CONHC_6H_5 \\ SO_2NHC_6H_5 \end{matrix},$$

and that of the anil by the formula,

$$C_6H_4 \begin{matrix} CO \\ SO_2 \end{matrix} N.C_6H_5.$$

The evidence for these formulæ is as follows: Orthotoluenesulphone chloride with aniline, gives a compound of the structure,

$$C_6H_4 \begin{matrix} CH_3 \\ SO_2.NHC_6H_5 \end{matrix};$$

on oxidation this passes over to the acid,

$$C_6H_4 \begin{matrix} COOH \\ SO_2.NHC_6H_5 \end{matrix},$$

which with phosphorus pentachloride goes over to the anil, which can hardly have any other structure than that indicated by the formula

$$C_6H_4 \begin{matrix} CO \\ SO_2 \end{matrix} N.C_6H_5.$$

Now this is identical in every particular with that obtained

[1] Ibid. 17, 347.

from the solid chloride, and when boiled with aniline, it goes over into the anilide derived from that chloride, which, therefore has the formula

$$C_6H_4 \begin{matrix} \diagup CO.NHC_6H_5 \\ \diagdown SO_2.NHC_6H_5 \end{matrix}.$$

It follows therefore that, in all probability, this chloride has the structure indicated by the formula

$$C_6H_4 \begin{matrix} \diagup COCl \\ \diagdown SO_2Cl \end{matrix}.$$

The work of Remsen and Saunders,[1] adduced additional evidence that this is the correct formula for this chloride.

When concentrated ammonia is shaken with the mixed chlorides, the liquid chloride is readily decomposed, the solid chloride being but slightly attacked. Mr. A. D. Chambers, of this laboratory, found that the product formed from the liquid chloride was ammonium orthocyanbenzenesulphonate,

$$C_6H_4 \begin{matrix} \diagup CN \\ \diagdown SO_3NH_4 \end{matrix}.$$

Mr. McKee has found that the pure liquid chloride forms the same compound, together with a small quantity of saccharine. It is difficult to understand the formation of this cyansulphonic acid under these conditions, except on the assumption of the formula

$$C_6H_4 \begin{matrix} \diagup CCl_2 \diagdown \\ \diagdown SO_2 \diagup \end{matrix} O$$

for the liquid chloride.

If this be the correct formula for this chloride, the formula of the anilide derived from it follows, and should be written thus:

$$C_6H_4 \begin{matrix} \diagup \\ \diagdown SO_2 \end{matrix} \begin{matrix} C \begin{matrix} \diagup NHC_6H_5 \\ \diagdown NHC_6H_5 \end{matrix} \\ \diagdown \diagup O \end{matrix}$$

Remsen and Kohler[2] found that the infusible anilide was a remarkably stable body towards reagents. The first evidence obtained which indicated that there had not been a

[1] *Loc. cit.* [2] *Loc. cit.*

deep-seated change in the arrangement of the constituent elements, was from the reaction between it and benzoyl chloride, by which benzanilide was formed. The other products of this reaction were not isolated.

They further ascertained that this anilide was acted on by phosphorus oxychloride, and by phosphorus pentachloride, though the products formed were not studied.

It was, primarily, with the hope of being able to clear up the nature of these reactions, that this investigation was begun. The results arrived at are given below. For convenience, the chlorides are spoken of as solid and liquid respectively, and the anilides as fusible and infusible.

II. Preparation of Material.

As the method now in use, devised by Mr. S. R. McKee, differs somewhat from that heretofore described for preparing the mixed chlorides, it is given in detail. The dry acid potassium salt prepared from commercial saccharine is mixed, in finely powdered condition, with phosphorus pentachloride, in the ratio of one molecule of the salt to two and a half molecules of the pentachloride. After the action has ceased the phosphorus oxychloride is distilled off under diminished pressure, or in an open dish on the water-bath. The oily residue is then washed two or three times with cold water, by thoroughly agitating the mixture in a wide-mouthed glass cylinder, with a conveniently bent glass rod. The oily chlorides, as free from water as possible, are then transferred to a beaker, placed in a freezing-mixture, and constantly stirred till the oil has solidified. The stirring is necessary to prevent the solidifying mass from adhering to the beaker. In this solid condition it is ground fine in a previously cooled mortar, transferred to a filter, and washed entirely free from the acids of phosphorus by use of ice-water. If care be taken to avoid contact with any warm body, the chlorides may be pressed almost completely dry between folds of filter-paper. They should be kept in a dessicator till required for use.

III. The Action of Water on the Mixed Chlorides.

Remsen and Saunders[1] found that both chlorides were de-

[1] Am. Chem. J., **17**, 350.

composed by water, forming the free acid together with hydrochloric acid, but they noted no difference in the rate of decomposition for the two substances. To test this point, 2 grams of the mixed chlorides were placed in 150 cc. cold water, and allowed to stand at the temperature of the room for seventeen days, being thoroughly shaken from day to day. The insoluble residue was then filtered off, washed with cold water, and carefully dried. It weighed 0.41 gram, and, without crystallizing, gave a melting-point of 74°–75° C. uncorr. Hence it was almost the pure solid chloride.

IV. The Action of Aniline on the Chlorides.

As already mentioned, Remsen and Coates, and later Remsen and Kohler also, studied the action of aniline on the mixed chlorides, and described the products formed.

Thinking one of the chlorides might be more readily acted on than the other, the following experiments were made, with the results named below :

1st. To a weighed quantity of the chlorides in 100 cc. water aniline was added in the ratio of one molecule aniline to one of the chlorides. After standing for twenty-four hours, with frequent shaking, crystals of each of the two anilides were obtained from the products formed, and some of the mixed chlorides had not been decomposed. Aniline hydrochloride was also formed.

2nd. In this experiment the ratio of the aniline to the chlorides was two molecules of the former to one of the latter, and the temperature of the water was kept at zero for the first three hours after mixing the compounds. Besides aniline hydrochloride, both anilides were formed and some of the solid chloride was still unacted on. But from the experiment with water and the chlorides, above described, the presence of the solid chloride only may have been due to the fact that the liquid chloride, not acted on by the aniline, had been decomposed by the water, as the products formed remained in the water five days before being examined.

3d. The chlorides were next treated with aniline in the ratio of four molecules of the latter to one of the former, but ether was used as the menstruum, in place of water. Much heat

was given out during the reaction, so the ether was kept cool by means of cold water. The products formed were the two anilides and aniline hydrochloride. Chloroform and benzene were tried as solvents in which to effect the reaction, the relative quantities of the aniline and the chlorides being the same as with ether as the solvent. In each case the products formed were the same as when ether was used.

As the yield seemed better when these solvents were used than when the two compounds were brought together in emulsion in water, the use of ether was adopted for preparing the anilides used in the investigation. The method used is here given in detail:

25 grams of the mixed chlorides are dissolved in absolute ether in a 500 cc. Erlenmeyer flask. 38.9 grams aniline, also in solution in absolute ether, are added slowly to the chlorides, the solution being constantly stirred. The temperature of the solution is to be kept down by placing the flask in cold water. A white precipitate appears as soon as any aniline is added. When the reaction is over, the ether is distilled off on the water-bath, but this does not proceed smoothly, owing to the insoluble products of the reaction. To avoid bumping, the flask should be shaken constantly while the distillation proceeds. Even then bumping is not entirely avoided.

The yellowish-white residue contains the mixture of the two anilides with aniline hydrochloride. Sometimes the residue has an oily appearance, and usually contains a slight excess of aniline. Cold water acidulated with hydrochloric acid is then added, the residue thoroughly stirred, and allowed to stand several hours. This treatment removes the aniline salts, and leaves the mixture of the two anilides. Some of the infusible anilide will be dissolved in the water with the salts of aniline, hence, this should be recovered by evaporating the water to a small volume, when the anilide will crystallize, leaving the aniline hydrochloride in solution. This anilide is quite frequently colored, but may be purified by boiling with animal charcoal in dilute alkaline solution.

To separate the two anilides the following method may be used: The mixture is dissolved in hot alcohol, and this solution is cooled as rapidly as possible by putting the vessel in

cold water. Under these conditions the fusible anilide crystallizes in thin white needles, while the infusible variety always crystallizes as short thick prisms. By rotating the vessel the fusible anilide will be disseminated through the alcohol, and may be poured off from the infusible prisms which will quickly settle to the bottom.

By proceeding as above described there is usually formed a small amount of the anil, and sometimes a considerable quantity of it appears. Since this is insoluble in cold dilute solution of sodium hydroxide, while the anilides are soluble in that reagent, the latter may be readily separated from the former by that means.

If the molecule of alcohol with which the infusible anilide crystallizes from solution in alcohol is undesirable, the crystals should be dissolved in dilute solution of sodium hydroxide, and the solution acidified, when the anilide will crystallize without water or alcohol of crystallization.

V. Action of Phosphorus Oxychloride on the Infusible Anilide.

Remsen and Kohler[1] observed that phosphorus oxychloride acted on the infusible anilide, but none of the products were isolated.

Since phosphorus oxychloride attacks rubber or cork stoppers, the following expedient was resorted to: A small condenser was fitted over the neck of a tubulated retort. Such an apparatus may be used for regular distillation, or where a return condenser is desired, as was the case in this experiment. The infusible anilide is then boiled with an excess of the oxychloride, until all the anilide is dissolved. This is attended by liberation of hydrochloric acid, and the solution becomes quite yellow. When the reaction is complete, the excess of the oxychloride is removed by distillation under diminished pressure. There is left in the retort a light-brown viscous liquid. While still warm the retort is turned about so that this residue is spread over as much surface as possible. Water is then added, and the retort set aside until the brown viscous mass has disappeared. There remains an insoluble almost

[1] Am. Chem. J., 17, 343.

white material, which dissolves in hot alcohol, forming a yellow solution. After repeated crystallization it melts sharply at 189.5°C. uncorr. An analysis of this product gave the following results:

I. 0.2002 gram gave 0.4997 gram CO_2 and 0.078 gram H_2O.
II. 0.2015 " " 0.5020 " " " 0.0795 " "
III. 0.2443 " " 0.1645 " $BaSO_4$.
IV. 0.1683 " " 0.1132 " "

	Calculated for $C_{19}H_{14}N_2SO_2$.	Found. I.	II.	III.	IV.	V.	VI.	VII.
C	68.22	68.07	67.95	...	...	...	...	...
H	4.20	4.33	4.39	...	...	...	...	...
S	9.59	...	...	9.24	9.25	...	...	...
N	8.41	...	...	...	...	8.63	8.61	8.5

The combustions were made by the lead chromate method, as described by deRoode,[1] the sulphur determinations by the method of Carius, while the nitrogen determinations were made by the absolute method, excepting the last one given (VII), which Mr. E. Mackay, in this laboratory, kindly made for me by the method of Kjeldahl.

Considerable difficulty was experienced in obtaining satisfactory results for carbon, although the appearance and the melting-point of the compound indicated its purity. Afterward a possible explanation was found in the fact that some of the anil described by Remsen and Coates,[2] was found to result under the conditions of the experiment. Its formation will be explained below.

When pure this compound is of bright lemon-yellow color, and the crystals obtained from alcohol are beautifully formed arborescent plates, very brittle. It is only slightly soluble in ether, or chloroform, but is readily soluble in benzene, glacial acetic acid, and acetone. When crystallized from either of the last two solvents named, monoclinic prisms of great brilliancy are obtained, the faces developed being usually ∞P, $\infty P\bar{\infty}$, oP, P, and $2P\bar{\infty}$.

2. *On the Fusible Anilide.*—This same compound is formed by the action of phosphorus oxychloride on the fusible anilide, the details of the experiment being the same as with the infu-

[1] Am. Chem. J., **12**, 226. [2] Ibid, **17**, 321.

sible anilide, given above. Some anil is formed in this case also.

Efforts to get a crystallized product from the brown viscous residue, by using various solvents, were unsuccessful. It appears that this residue is really a solution of the yellow product in phosphoric acid, from the following consideration: To a small amount of phosphoric acid prepared by adding a very little water to phosphoric anhydride, was added some of the pure yellow product, and the mixture was then heated. A clear solution was effected, having the same consistency and color as the residue obtained above; and when water was added to this, it decomposed in much the same way.

If the empirical formula arrived at by analysis of this yellow product be compared with that of the anilide, from which it is derived, the equation,

$$C_{19}H_{16}SO_3N_2—H_2O=C_{19}H_{14}SO_2N_2,$$

shows their relation. It thus appears as if the action of the oxychloride is one of dehydration.

VI. The Action of Phosphorus Pentoxide.

1. *On the Infusible Anilide.*—It seemed reasonable to expect the same compound to result if either of the anilides should be treated with a strong dehydrating agent. Accordingly, some infusible anilide was mixed with phosphorus pentoxide in a test-tube and then heated for two hours in an air-bath to 130°–150°, the test-tube being closed by a Bunsen valve. The mass had become slightly yellow in color. When cold, water was added to dissolve the phosphoric acid and anhydride, and the portion insoluble in water was found to have the same crystalline form, when deposited from alcohol, and to melt at the same temperature, as the product from the other experiments already described, using the oxychloride of phosphorus.

2. *On the Fusible Anilide.*—If the fusible anilide be treated with phosphorus pentoxide, as just described, the same yellow compound is formed.

Neither acetyl chloride nor acetic anhydride effect this dehydration of the anilide.

Hoogewerff and Van Dorp[1] have described the formation of

[1] Rec. Trav. Chim., **12**, 12; also **13**, 93.

some iso-imides, by treating dibasic acid derivatives of the general formula,

$$R\begin{cases}CONHR'\\COOH\end{cases},$$

with either acetyl chloride, or phosphorus oxychloride, the reaction with the former being represented by the equations,

$$R\begin{cases}CONHR'\\COOH\end{cases}+CH_3COCl=R\begin{cases}C\overset{N\text{-}R'}{\diagdown\!\!\diagup}OH\\COOH\end{cases}+CH_3COCl=$$

$$R\begin{cases}C=N.R'\\CO\diagup\diagdown O\end{cases}+CH_3COOH+HCl.$$

[Iso-imides.]

With the oxychloride of phosphorus the reaction would be analogous. In all cases examined, R' was $.CH_3$, $.C_2H_5$, or $.CH_2.C_6H_5$, while R was the residue of camphoric, and phthalic acids respectively. Clearly the rôle of the oxychloride in these reactions was the same as that which it plays in the reactions with the anilides. The equation,

$$3C_6H_4\begin{cases}CONHC_6H_5\\SO_2NHC_6H_5\end{cases}+POCl_3=3C_6H_4\begin{cases}C=N.C_6H_5\\SO_2\end{cases}N.C_6H_5+$$

$$H_3PO_4+3HCl,$$

then represents the reaction with the fusible anilide.

3. *Structure of this Compound.*—From the methods of formation already described, especially those involving the use of the fusible anilide, the formula for which is entirely satisfactorily represented as above, it naturally follows that the formula,

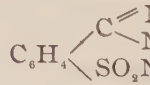
$$C_6H_4\begin{cases}C=N.C_6H_5\\SO_2\end{cases}N.C_6H_5,$$

correctly represents the structure of this new compound. It thus appears to be a dianil of orthosulphobenzoic acid.

Jesurun[1] obtained this same compound by the action of ani-

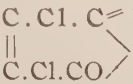
[1] Ber. d. chem. Ges., **26**, 2292.

line on orthocyanbenzenesulphone chloride. He thinks the first product formed is a benzamidine-sulphanilide,

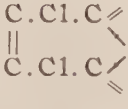


and that this loses ammonia, forming this dianil, to which he gives the same structural formula as above assigned.

The grouping of the two aniline residues in this dianil is the same as that given by Anschütz and Beavis[1] for the dichlormaleic dianil, the formula of which is,



which is formed by the action of aniline on dichlormaleicanildichloride,



prepared by the action of phosphorus pentachloride on succinanil.[2]

It seems reasonable to expect the formation of the analogous derivatives of the anil described by Remsen and Coates. Preliminary experiments have been made with this end in view, but as yet witnout success. The problem is still under investigation.

4. *Chemical Properties of the Dianil.*—(*a*) It was mentioned above that this compound may be crystallized from glacial acetic acid. For this purpose the solution must not be heated longer than is necessary to effect solution. If the solution be boiled for two or three hours in a flask connected with a reflux condenser, none of the dianil will separate on cooling, but instead there will appear slender white needles. These are crystals of the infusible anilide. The identity was established by the melting-point, crystalline form when recrystallized from alcohol, and from water, ready solubility in dilute cold alkaline solution, from which the characteristic

1 Ber. d. chem. Ges., **28**, 58.
2 Ann. Chem. (Liebig). **263**, 156.

granular crystals of the infusible anilide separate when the solution is acidified. The infusible anilide itself assumes the acicular habit if crystallized from glacial acetic acid. To further test the identity some of these needles were treated with phosphorus oxychloride, and the dianil together with some of theordinary anil was obtained, just as when the granular infusible anilide was used.

This conversion of the dianil into the infusible anilide is accompanied by a change in color of the acetic acid solution, from a darker to a much lighter shade of yellow. This reaction is represented by the equation,

$$C_6H_4\begin{cases} C=N.C_6H_5 \\ SO_2 \end{cases} N.C_6H_5 + H_2O = C_6H_4\begin{cases} C<_{NHC_6H_5}^{NHC_6H_5} \\ SO_2 \end{cases} O.$$

The yield is quantitative.

(*b*) The crystals of the dianil may be boiled with a water solution of sodium hydroxide, either dilute or strong, without being affected in any way. When boiled for about an hour with alcoholic potash, a solution of the dianil is effected. If now the alcohol be evaporated almost completely, there is no precipitate formed on addition of water. If, however, the solution be acidified, crystals of the infusible anilide separate on standing, provided the solution be sufficiently dilute. If the solution be quite concentrated, the anilide will be precipitated at once by the acid.

The effect of boiling the dianil with alcoholic potash is to induce the dianil to unite with the elements of water to form the infusible anilide. It is worthy of note that these elements arrange themselves in the more stable grouping of the infusible, rather than the fusible anilide, which is less stable.

(*c*) When concentrated hydrochloric acid is added to the dianil the yellow color of the latter changes from yellow to white. If the acid be filtered off at once, and the residue washed with cold water, the yellow color reappears. If, however, the dianil be boiled with the acid for about an hour the insoluble residue will be found to remain white after removing the acid completely, and when crystallized from alcohol it forms slender white needles. These are crystals of

the anil described by Remsen and Coates.[1] In the hydrochloric acid solution is some aniline hydrochloride. This reaction may be represented by the equation,

$$C_6H_4\begin{cases} C = N.C_6H_5 \\ SO_2 \end{cases} N.C_6H_5 + H_2O + HCl = C_6H_4\begin{cases} CO \\ SO_2 \end{cases} N.C_6H_5 + C_6H_5NH_2.HCl.$$

It was mentioned above that some of this anil was always formed during the action of phosphorus oxychloride on the anilides. In the light of the above reaction its presence is explained, being due to a secondary reaction between the dianil and the hydrochloric acid.

VII. Action of Phosphorus Pentachloride on the Infusible Anilide.

When the infusible anilide is added slowly to a heated solution of phosphorus pentachloride in chloroform, reaction sets in at once, and generally the solution changes to a light yellow color. Usually about twice as much pentachloride as of the anilide is necessary to effect complete solution of the latter. In the first experiment tried, 2.5 grams of the pentachloride were used to one gram of the anilide, and the heating was continued only as long as was necessary to effect complete solution of the anilide. On cooling, radiating tufts of fine white needles separated, completely filling the liquid. More chloroform was added, and heat applied till all the needles were dissolved. But the needles did not separate again, even when almost all the chloroform had evaporated. The last traces of chloroform were then driven off by heating gently for some time, and the yellow viscous residue was treated as the brown residue from the oxychloride experiment (page 11). Some of the anil was found present, though the chief product was the yellow dianil. The final products of this reaction are the same as those formed by the action of phosphorus oxychloride on the infusible anilide.

This experiment was repeated under the same conditions as before, and under varied conditions, though always with-

[1] *Loc. cit.*

out obtaining those fine white needles. The final products were the same each time.

From the results of these experiments it will readily be seen that it is possible to pass from the fusible anilide to the infusible anilide, by passing first to the yellow dianil and then by boiling this with glacial acetic acid, or an alcoholic solution of potassium hydroxide, to the infusible anilide.

Again, from this dianil one may obtain the anil by boiling with concentrated hydrochloric acid. And since the anil, when boiled with aniline, passes over to the fusible anilide, it is therefore possible to pass in the opposite direction, from the infusible to the fusible anilide.

VIII. The Action of Benzoyl Chloride on the Infusible Anilide.

Five grams infusible anilide were boiled with an excess of benzoyl chloride until it had dissolved. The excess of the benzoyl chloride was removed as completely as possible by distillation under diminished pressure, and the residue boiled with water. After this water had become cold, and without separating it from the insoluble residue, sodium carbonate was added to alkaline reaction and the vessel was heated gently on the water-bath to about 60° C. This solution was then poured off from the undissolved residue and acidified, when benzoic acid was precipitated.

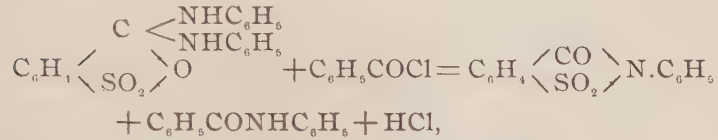
The residue insoluble in sodium carbonate solution was then dissolved in alcohol and boiled with animal charcoal. From this solution separated plates of a dirty yellow color, but which, when purified by repeated recrystallization, became white, and assumed the acicular habit, melting sharply at 190.5° uncorr. They proved to be the anil.

The mother-liquor from the above was then evaporated to dryness, and the residue boiled with about 750 cc. water, and this water, while still hot, was siphoned from the part insoluble in the water, which had melted to a brown oil. By repeatedly boiling this residue with water almost all of it was finally dissolved.

From this water, on cooling, a white precipitate was deposited. When crystallized from alcohol, this forms small

globular-shaped tufts of white needles, but these have not yet been identified, partly from lack of material, partly from lack of time.

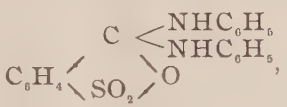
From the water filtrate from this white precipitate, after evaporating to a very small volume, a small quantity of benzanilide was obtained, which was identified by its melting-point, crystal form, and by comparison with a specimen of benzanilide. The equation,



represents the reaction so far as yet understood.

A second experiment gave the same results as the one just described. No trace of the product mentioned by Remsen and Kohler,[1] as giving rise to the infusible anilide on addition of aniline, was obtained in either case. It is possible that this product might be isolated by keeping the temperature as low as possible in order to effect the reaction.

IX. *Structure of the Infusible Anilide.*—From the results obtained in this investigation it is clear that the two aniline residues are intact in the infusible anilide. This fact, together with the further fact that this anilide is derived only from the liquid, or unsymmetrical chloride, by the action of aniline, leaves but little if any doubt that the structure of this anilide is correctly represented by the formula,



first proposed by Remsen and Coates.[2]

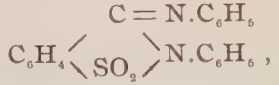
X. Conclusion.

The results arrived at in this investigation may be briefly summarized as follows:

1. Water decomposes the liquid chloride more readily than the solid chloride.

[1] Am. chem. J., **17**, 342. [2] *Ibid*, **17**, 320.

2. Orthosulphobenzodianil, having the structure represented by the formula,



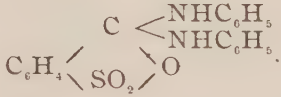
is obtained by the action of phosphorus oxychloride or phosphoric anhydride on either anilide, and by the action of phosphorus pentachloride on the infusible anilide.

3. The infusible anilide is reformed from this dianil on boiling with glacial acetic acid or with alcoholic potash.

4. The anil of orthosulphobenzoic acid is obtained by boiling this dianil with concentrated hydrochloric acid.

5. Benzoyl chloride acts on the infusible anilide, forming benzanilide and the anil of orthosulphobenzoic acid.

6. The two aniline residues are intact in the infusible anilide, and this anilide has the structure represented by the formula,



Biographical.

The author was born near Apex, Wake Co., N. C., June 6th, 1865. His early education was received in private schools in that village. He entered Wake Forest College, N. C., September, 1881, receiving the degree of Bachelor of Arts in 1885. For three succeeding years he taught in private schools in his native State. He returned to Wake Forest College, September, 1888, and received the degree of Master of Arts in June, 1889. In October of that year he entered the Johns Hopkins University, remaining two years. During the two years 1891–93, he taught in the Wisconsin State Normal School, located at Oshkosh. Since October, 1893, he has continued his work at the Hopkins University. His subjects have been Chemistry, Mineralogy, and Physics.